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ADSORPTION OF ENROFLOXACINE ON NATURAL ZEOLITE - CLINOPTILOLITE

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The potential use of Croatian natural zeolite - clinoptilolite as alternative adsorbents for removal of enrofloxacin (ENRO) as model pollutant was studied in a batch system. The influence of contact time and initial ENRO concentration on the sorption process was investigated. The percentage removal of ENRO from aqueous phase decreased with an increase in initial concentration. The experimental data were analyzed using the pseudo-second-order kinetic model. The equilibrium adsorption data were analyzed using two widely applied isotherms: Langmuir and Freundlich isotherm models. A linear method was used for comparing the best fitting of the isotherms. The little bit better fit was found to be Langmuir isotherm for adsorption of ENRO onto natural zeolite. The maximum ENRO capacity of natural zeolite from the Langmuir isotherm model at 318 K was 2.4307 mg/g.
Key words: enrofloxacin, adsorption isotherms, kinetics of sorption, natural zeolite.

Adsorpcija enrofloksacina na prirodni zeolit – klinoptilolit. U ovom radu ispitana je mogućnost primjene hrvatskog prirodnog zeolita - klinoptilolita kao alternativnog adsorbensa za uklanjanje enrofloksacina (ENRO) statičkim tzv. "batch" postupkom. U radu je ispitivan utjecaj početne koncentracije ENRO i vremena kontakta otopine ENRO i zeolita na proces adsorpcije. Rezultati su pokazali da se povećanjem početne koncentracije smanjuje količina uklonjenog enrofloksacina. Eksperimentalni rezultati analizirani su uporabom kinetičkog modela pseudo-drugog reda. Dobiveni podaci analizirani su uporabom dvije sorpcijske izoterme: Langmuir-ove i Freundlich-ove. Parametri izotermi procijenjeni su linearnom regresijom. Malo bolje slaganje s eksperimentalnim rezultatima sorpcije ENRO na prirodni zeolit postignuto je Langmuir-ovom izotermom. Maksimalni kapacitet vezanja ENRO na prirodni zeolit prema Langmuir-ovoj izotermi kod 318 K iznosi 2,4307 mg/g.
Ključne riječi: enrofloksacin, adsorpcijske izoterme, kinetika sorpcije, prirodni zeolit.

INTRODUCTION

In the 1970s pharmaceuticals were detected in the environment. During the 1980s not much interest was shown towards this issue. Since the middle of the 1990s, awareness of pharmaceuticals in the environment has been growing [1].

Pharmaceuticals can enter the environment through two major sources: from human and veterinary use (Figure 1).

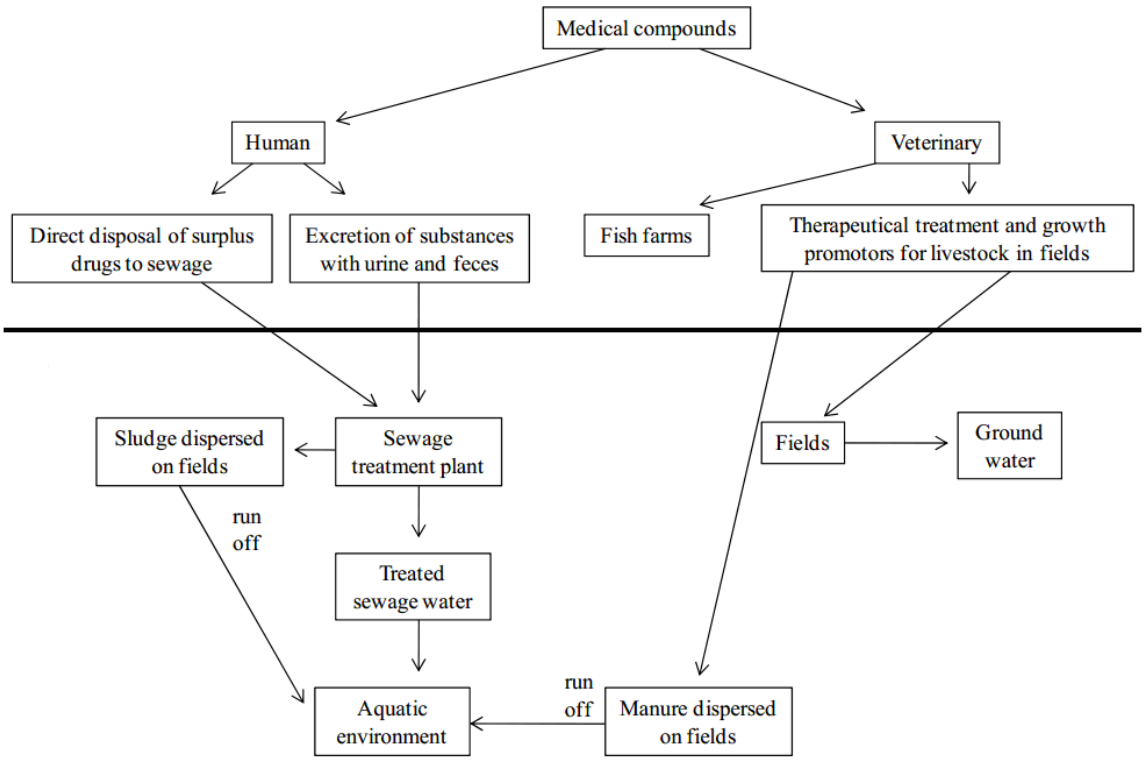

Figure 1. Entry of both human and veterinary drugs in the environment (adapted from [2])
Slika 1. Ulaz humanih i veterinarskih lijekova u okoliš (preuređeno prema [2])

Pharmaceuticals and related products have become chemicals of emerging environmental concern in recent years [3]. Pharmaceuticals, especially antibiotics, have been used in human medicine to treat or prevent microbial infections, and as veterinary drugs and husbandry growth promoters in aquaculture and livestock operations [2]. Veterinary antibiotics have been shown to cause oxidative damage in liver cells of rainbow trout (*Oncorhynchus mykiss*) [4], and were lethal to brine shrimp (*Artemia*) [5].

Enrofloxacin, oxytetracycline, and florfenicol are among the most commonly used antibiotics during shrimp cultivation and are commonly mixed into food pellets; however, the inappropriate use of these compounds can result in accumulation of residual antibiotic in tissue and contribute to the emergence of resistant bacteria *via* residual antibiotics persisting in the sediment.

Enrofloxacin (ENRO) is a fluoroquinolone antibiotic, which is widely used in poultry production in order to treat respiratory and enteric bacterial infections. So, ENRO occurs widely in natural waters because of its extensive use as a veterinary chemotherapeutic agent. ENRO is nalidixic acid derivative with broad-spectrum activity against Gram-negative bacteria. The core structure is a dihydroquinoline or 4-quinolone ring; this structure is lipophilic and has a low molecular weight, promoting tissue penetration [6, 7].

Nowadays, the presence of antibiotic active compounds as pollutants in the aquatic environment is considered as relevant and very important topic because

their presence in natural waters contributes to the spread of antibiotic resistance in microorganisms. Therefore, their detection, investigation of their effects and discovery of versatile possibilities to remove them from the environment impose challenges for researchers [8].

Zeolites are crystalline, naturally occurring hydrated aluminosilicate minerals and belong to the class of minerals known as tectosilicates. The structures of zeolites consist of three-dimensional frameworks of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra. The aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation (sodium, potassium or calcium). These cations are exchangeable with different cations in solutions [9]. These features make zeolite very attractive from the aspect of water cleaning technology. Clinoptilolite is the most abundant natural zeolite and can be used as ion exchanger or sorbent for inorganic or organic compounds [9-14].

Effluent from pharmaceutical wastewater normally treated using flocculation, flotation, coagulation, filtration, settling, ion exchange, carbon adsorption, air stripping, advanced oxidation processes (AOPs), reverse osmosis, biological treatment (using trickling filters, anaerobic, activated sludge, and rotating biological contactors) as well as combined chemical-biological treatment [15-17].

Adsorption is one of the few promising alternatives for this purpose, especially using low-cost natural sorbets such as zeolite, biomass, agricultural wastes, and clay materials. Zeolite-based adsorbents have satisfactory adsorption capacity, low cost and without any highly sophisticated instruments. They are abundant in nature, and they are not toxic. Also, some work found that ozone at sufficient concentrations over specified time periods was able to decompose the enrofloxacin adsorbed on zeolite [7]. That fact, gives opportunity of reusing of zeolite for the adsorption or for some other purposes like: ammonium ion removal in waste stream treatment, sewage treatment, pet litter and aquaculture, odor control, heavy metal ion removal from nuclear, mine and industrial wastes, and in agricultural use, such as soil conditioner and animal feed supplement [18-20].

The purpose of this study is to investigate the possible usage of Croatian natural zeolite clinoptilolite for removal of enrofloxacin (ENRO). Deposit of clinoptilolite-rich tuff in Croatia occurs in porous sedimentary rocks of Donje Jesenje, near Krapina. We hope that this research will contributed to the application of this natural mineral in prevention and reducing of natural waters pollution.

MATERIALS AND METHODS

Adsorbent

The tested natural zeolite - clinoptilolite originates from the mine Donje Jesenje, Croatia, where it was ground and separated into fraction with particle sizes less than 150 μm. Chemical composition of natural zeolite was determined by the standard chemical analysis for alumosilicates and results in mass % are SiO_2-64.93; Al_2O_3-

13.39; Fe_2O_3-2.07; Na_2O-2.40; K_2O-1.43; CaO-2.00; MgO-1.08; loss by ignition at 1000 °C-9.63.

X-ray diffraction (XRD) analysis was performed by PHILIPS PW 1010 diffractometric system (CuKα radiation, 2θ = 3- 60 °) on natural sample to confirm the mineral identity of the zeolites. The zeolite obtained from a deposit in Donje Jesenje was stated to be of 40%-50% purity on clinoptilolite, while the impurities included illite, feldspar, quartz and muscovite [11].

Adsorbate

High purity (> 98%) enrofloxacin (ENRO) was supplied from Veterina (Kalinovica, Croatia). A stock solution of ENRO was prepared (100 mg/L) by dissolving a required amount of ENRO powder in MilliQ water. The stock solution was diluted with MilliQ water to obtain desired concentration ranging from 1 to 20 mg/L. The chemical structure of ENRO is shown in Figure 2.

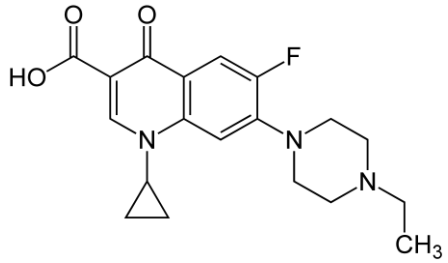

Figure 2. Chemical structure of enrofloxacin, *M*r = 359.39 [C_{19} H_{22} F N_3 O_3] (1-Cyclopropyl-7-(4-ethyl-1-piperazinyl)-6-fluoro-1,4-dihydro-4-oxo-3-quinolonecarboxylic acid)
Slika 2. Kemijska struktura enrofloksacina, *M*r = 359,39 [C_{19} H_{22} F N_3 O_3] (1-ciklopropil-7-(4-etil-1-piperazinil)-6-fluoro-1,4-dihidro-4-okso-3-kinolonskokarboksilna kiselina)

Batch adsorption experiments

First set of experiments were performed to determine the contact time required for equilibrium sorption of ENRO. For this purpose, 0.150 g zeolite has been equilibrated with 15.0 mL of the 20 mg ENRO/L at 25 °C during a time interval between 1 and 60 min.

Second set of experiment were performed in order to investigate effect of initial concentration on sorption process of ENRO on natural zeolite. Initial ENRO concentration was: 1, 2, 5, 10, 15 and 20 mg/L; time of contact was 5 min. Suspensions were shaken at 25 °C in an INNOVA 4080 shaker at rotation speed of 200 rpm. After shaking in a thermostatic system, the solid phase was separated from the solution by filtration (Whatman blue ribbon filter), and ENRO concentration was determined in the liquid phase. The concentration of ENRO in the experimental solution was determined from the calibration curve prepared by measuring absorbance of calibration ENRO solutions in the concentration range from 1 to 20 mg/L at λ_{max} 270 nm using an UV–Vis Spectrophotometer (PERKIN ELMER Lambda 35, USA).

The difference between the initial and equilibrium mass concentrations of

ENRO is used for calculation of the quantity of ENRO adsorbed on unit mass of natural zeolite-clinoptilolite (q, mg ENRO/g of the zeolite), taking into consideration the data related to the zeolite weight, volume and mass concentration of the solution. The amount of ENRO adsorbed onto natural zeolite was calculated by using the following expression:

$$q_e = \frac{(\gamma_0 - \gamma_e)}{m} \cdot V \qquad (1)$$

where q_e is the equilibrium sorption capacity of ENRO adsorbed *per* unit mass of the natural zeolite (mg/g); γ_0 and γ_e are the initial ENRO concentration and ENRO concentration at equilibrium (mg/L), respectively; V is the volume of the ENRO solution (L); and m is the mass of the adsorbent-natural zeolite (g).

The removal efficiency (E, %) and distribution ratio (K_D, L/g) were calculated using the equations (2) and (3):

$$E = \frac{\gamma_0 - \gamma_e}{\gamma_0} \times 100 \qquad (2)$$

$$K_D = \frac{\text{amount of ENRO in adsorbent}}{\text{amount of ENRO in solution}} \times \frac{V}{m} = \frac{\gamma_0 - \gamma_e}{\gamma_e} \times \frac{V}{m} \qquad (3)$$

Equilibrium isotherm modelling

Adsorption isotherms are preconditions for understand the nature of the interaction between adsorbate and the adsorbent used for the removal of organic pollutants in wastewater. To investigate an interaction of adsorbate molecules (ENRO) and adsorbent surface (natural zeolite - clinoptilolite) two well-known models, the Freundlich [21] and Langmuir [22] isotherms, were selected to explicate ENRO – zeolite interaction in this study.

Freundlich isotherm

The Freundlich isotherm describes the non-ideal adsorption of a heterogeneous system and reversible adsorptions in which it is characterized by the heterogeneity factor $1/n$ [21]. The model can be expressed as

$$q_e = K_F \cdot \gamma_e^{1/n} \qquad (4)$$

where q_e is the amount of ENRO adsorbed per unit of adsorbent - zeolite (mg/g), γ_e is the concentration of ENRO at adsorption equilibrium (mg/L), K_F ((mg/g)(L/mg)$^{1/n}$)) and n are the Freundlich constants related to the sorption capacity and sorption intensity, respectively.

Eq. (4) can be linearised by taking logarithms:

$$\log q_e = \log K_F + \frac{1}{n} \log \gamma_e \qquad (5)$$

A log q_e - log γ_e plot should yield an intercept of log K_F and a slope of $1/n$.

Langmuir isotherm

The Langmuir model is valid for monolayer sorption onto a surface with a finite number of identical sites. It is represented by the equation (6):

$$q_e = \frac{q_m K_L \gamma_e}{1 + K_L \gamma_e} \quad (6)$$

where q_e is the equilibrium adsorption capacity (mg/g), γ_e is the equilibrium liquid phase concentration (mg/L), q_m is the maximum adsorption capacity (mg/g) and K_L is adsorption equilibrium constant, (L/mg). The Langmuir model in linear form:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m \gamma_e} \quad (7)$$

Langmuir parameters (q_m and K_L) can be determined from the linear plot of $1/q_e$ against $1/\gamma_e$ with slope $1/q_m$ and intercept $\frac{1}{K_L q_m}$.

RESULTS AND DISCUSSION

Sorption kinetics

In this work natural zeolite from Donje Jesenje, Croatia was used in order to investigate its ability in removal of enrofloxacin from aqueous solutions, and has been examined in a batch adsorption process at 25 °C. Batch studies have been performed to describe the impact of enrofloxacin concentration and contact time on the removal of the enrofloxacin. The experimental data were analyzed by the Langmuir and Freundlich isotherm models. The sorption parameters and the fitting of the models are determined by linear regression. The kinetics of the sorption is checked by pseudo-first- and pseudo-second-order models.

Effect of initial ENRO concentration and contact time

Figure 3 shows the effect of contact time on the amount of ENRO removed by natural zeolite.

Results presented in Figure 3 show that the sorption increasing very fast in first 2 min, equilibrium is achieved at about 5 min and after that amount of sorbed ENRO on zeolite is not change significantly. Figure 4 show the effect of initial concentration on the removed amount of ENRO, time of contact was 5 min. Figure 5 represents the removal efficiency of ENRO by natural zeolite versus the initial concentration. The effect of the initial concentration of ENRO on the distribution ratio, K_D, is shown in Figure 6.

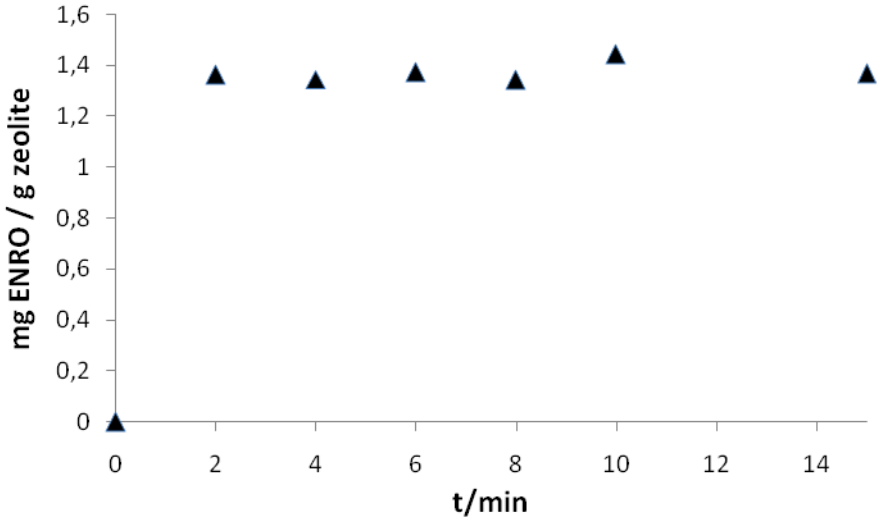

Figure 3. Adsorption of ENRO (20 mg/L) onto natural zeolite as a function of contact time
Slika 3. Adsorpcija ENRO (20 mg/L) na prirodni zeolit u ovisnosti o vremenu

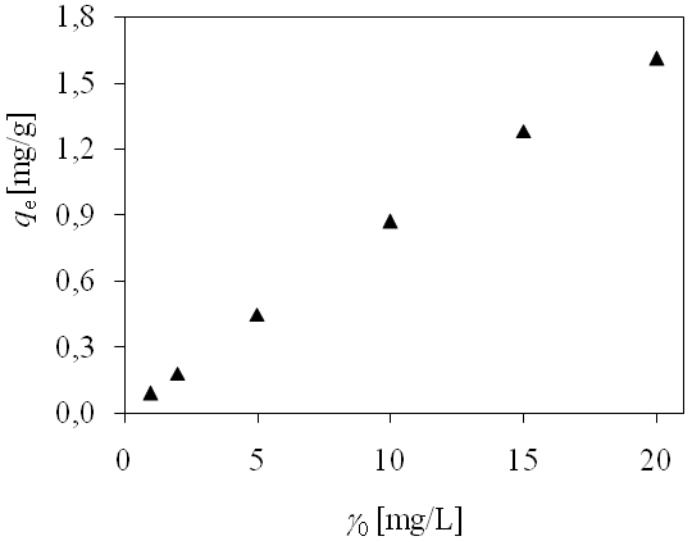

Figure 4. Sorption of ENRO by natural zeolite as a function of initial concentration;
m (zeolite) = 0.150 g; *V* (solution) = 15.0 mL
Slika 4. Sorpcija ENRO na prirodni zeolit kao funkcija početne koncentracije;
m (zeolita) = 0,150 g; *V* (otopine) = 15,0 mL

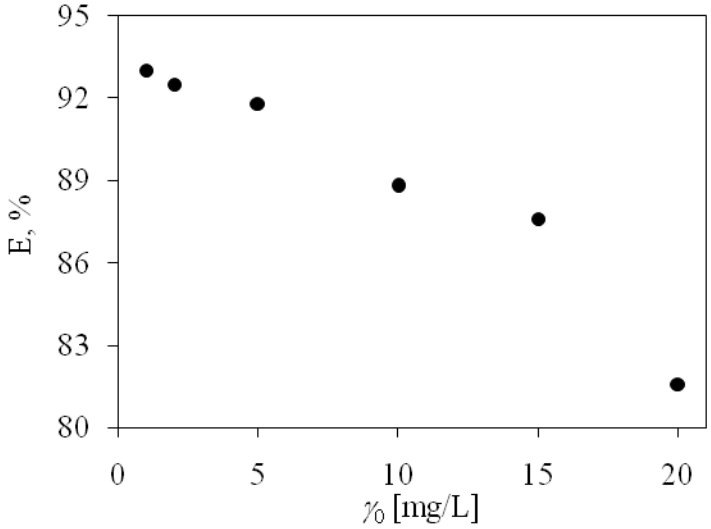

Figure 5. ENRO removal efficiency by natural zeolite as function of initial concentration; *m* (zeolite) = 0.150 g; *V* (solution) = 15.0 mL
Slika 5. Učinkovitost uklanjanja enrofloksacina iz otopine na prirodni zeolit kao funkcija početne koncentracije; *m* (zeolita) = 0,150 g; *V* (otopina) = 15,0 mL

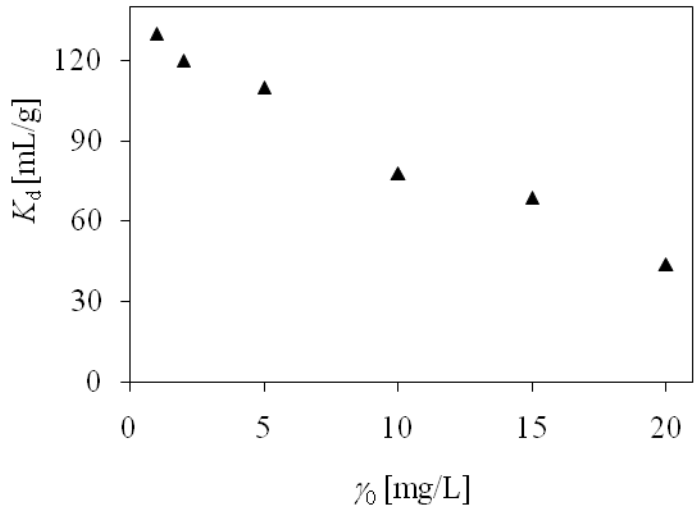

Figure 6. Effect of initial concentration of ENRO on distribution ratio of ENRO
Slika 6. Utjecaj početne koncentracije ENRO na konstantu raspodjele ENRO

The initial ENRO concentration was varied from 1 to 20 mg/L. At all initial ENRO concentrations investigated, the sorption occurs very fast initially. After 5 minutes of sorption process, the amount of sorption by natural zeolite reaches 3.7, 66.4, 263.3, 801.4, 1167.1 and 1542.4 μg ENRO/g zeolite for initial ENRO concentrations of 1, 2, 5, 10, 15 and 20 mg /L, respectively. The effect of initial antibiotic concentration was investigated under equilibrium conditions. ENRO removal efficiency tended to

decrease when increasing the initial ENRO concentration from 1 to 20 mg/L.

Pseudo-second-order equation

Several kinetic models are available to understand the behavior of the adsorbents and to examine the controlling mechanism of the sorption process. In the present investigation, the sorption data were analyzed using the pseudo-first-order and pseudo-second-order kinetic models.

The experimental data for the removal of ENRO when analyzed on the pseudo-first-order equation did not result in a perfect straight line when a plot was drawn between $\ln(q_e - q_t)$ and t indicating a non-fit on the model. The low correlation coefficient value, as obtained for the pseudo-first-order model, indicates that sorption of ENRO did not follow the pseudo-first-order kinetic model.

The pseudo-second-order equation is represented as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (8)$$

where k_2 is the rate constant of pseudo-second-order adsorption (mg/g min). Integrating Eq. (8) for the boundary conditions $q_t = 0$ to $q_t = q_t$ and $t = 0$ to t=t, the following equation is obtained:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (9)$$

t/q_t versus t. Slope = $1/q_e$, intercep t= $1/(k_2 q_e^2)$

A good linear plot of t/q_t against t for the pseudo-second-order kinetic model (Eq. (8)) shows a fit on the model (Figure 7).
Kinetics parameters for the sorption of ENRO by natural zeolite - clinoptilolite, as calculated from the linear plots of the pseudo-second-order kinetics models (Figure 7) are k_2 = 14.1843 g/mg min and q_e = 1.3860 mg/g.

The insufficiency of the pseudo-first-order model to fit the kinetics data could possibly be due to the limitations of the boundary layer controlling the sorption process. The experimental data were observed to fit well the pseudo-second-order equation. The high correlation coefficient value (R^2 = 0.9970), as obtained for the linear plot of t/q_t against t for the pseudo-second-order equation, was observed to be close to 1. This suggests that the process of sorption kinetics of ENRO by zeolite follows the pseudo-second-order equation and the process controlling the rate may be controlled by chemical sorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate.

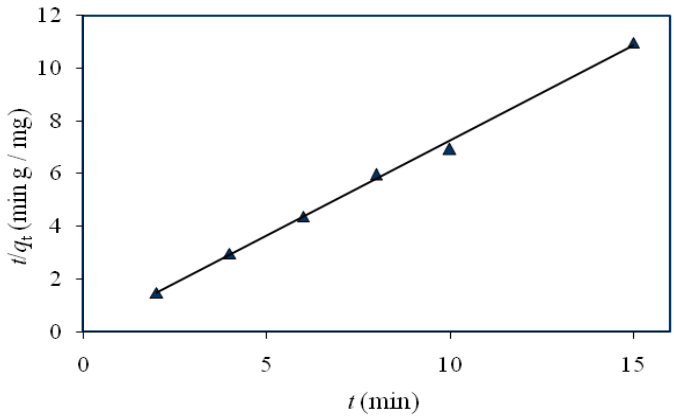

Figure 7. Linearized pseudo-second-order plots for the sorption of ENRO by natural zeolite.
Slika 7. Linearizirani graf sorpcije ENRO na prirodni zeolit prema kinetičkom modelu pseudo-drugog reda.

Equilibrium isotherm modelling

The linear plot of log q_e against log γ_e is shown in Figure 8A and the values of obtained Freundlich parameters are presented in Table 1. The Freundlich exponent, *n*, should have values lying in the range of 1 to 10 for classification as favorable adsorption. Table 1 show that *n* value is in the range of 1–10 for investigated adsorbent - zeolite.

Langmuir parameters q_e and K_L are determined from the linear plot of $1/q_e$ against $1/\gamma_e$ (Fig. 8B). The resulting straight line confirms that the Langmuir isotherm is followed in the monolayer sorption process (Figure 8B). The monolayer adsorption capacity was found to be 2.4307 mg ENRO/g natural zeolite. The values of calculated Langmuir parameters are presented in Table 1.

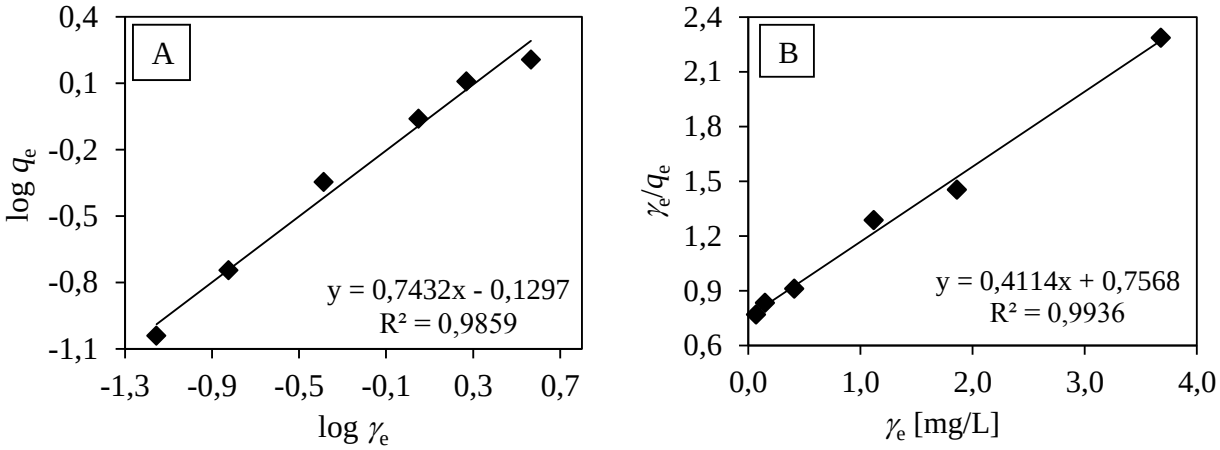

Figure 8. The linearized (A) Freundlich and (B) Langmuir adsorption isotherms for the sorption of ENRO by natural zeolite
Slika 8. Linearizirane (A) Freundlich-ova i (B) Langmuir-ova adsorpcijska izoterma za sorpciju ENRO na prirodni zeolit

Table 1. Isotherms parameters obtained using the linear method for the adsorption of ENRO onto natural zeolite at 298 K
Tablica 1. Parametri izotermi dobiveni linearizacijom krivulja adsorpcije ENRO na prirodni zeolit pri 298 K

Isotherm	Parameter	T = 298 K
Freundlich	n	1.3455
	K_F ((mg/g)(L/mg)$^{1/n}$))	0.7418
	R^2	0.9859
Langmuir	q_m (mg/g)	2.4307
	K_L (L/mg)	0.5436
	R^2	0.9936

The values of correlation coefficient for both sorption isoterms are nearly the same which means that both isoterms could be used to describe experimental sorption data (Table 1).

The essential characteristics of the Langmuir isotherm can be expressed by a separation or equilibrium parameter, a dimensionless constant, which is defined by equation (10) [23]:

$$R_L = \frac{1}{1+(K_L \gamma_0)} \quad (10)$$

where γ_0 is the initial ENRO concentration (mg/L) and K_L is the Langmuir constant (L/mg). The value of R_L indicates the type of the isotherm to be either unfavorable (R_L >1), linear (R_L = 1), favorable (0< R_L <1) or irreversible (R_L =0).

The values of R_L were found to be in the range of 0–1, indicating that the sorption process is favorable for zeolite as adsorbent (Figure 9).

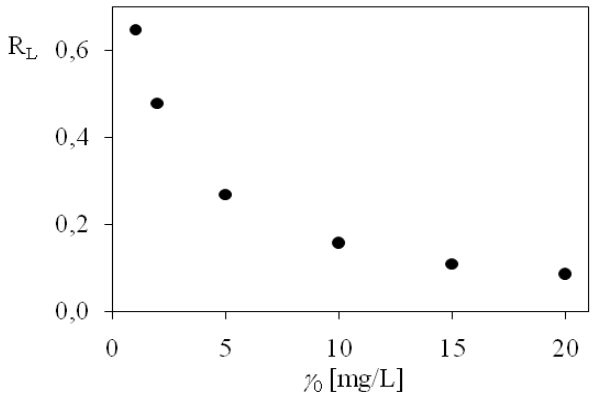

Figure 9. Values of separation factor R_L for sorption of ENRO by natural zeolite
Slika 9. Vrijednosti faktora separacije, R_L za sorpciju ENRO na prirodni zeolit

CONCLUSION

Batch studies at 25 °C have been performed to describe the impact of enrofloxacin concentration and contact time on the removal of the enrofloxacin from aqueous solutions on naturale zeolite – clinoptilolite. Obtained results indicate that sorption of ENRO on natural zeolite is very fast and equilibrium sorption was achieved in 5 min. In order to describe adsorption equilibrium data for enrofloxacin on zeolite Langmuire and Freundlich isotherms were used. Langmuir isotherm model gave a little bit higher value of correlation coefficient in comparison to Freundlich isotherm. The sorption parameters and the fitting of the models are determined by linear regression and the kinetics of the sorption followed pseudo-second-order model. The results of this study indicate that natural zeolite - clinoptilolite from Donje Jesenje, Croatia is an efficient, environmentally-friendly, low-cost and alternative material for the removal of antibiotic enrofloxacine from aqueous solutions.

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